Polyolefin membrane with integrally asymmetrical structure and process for producing such a membrane

Claims:

- Process for producing an integrally asymmetrical hydrophobic membrane having a sponge-like, open-pored, microporous support structure and a separation layer with a denser structure compared to the support structure, the process comprising at least the steps of:
 - a) preparing a homogeneous solution from a system comprising 20-90% by weight of a polymer component consisting of at least one polyolefin and 80-10% by weight of a solvent for the polymer component, wherein the system at elevated temperatures has a range in which it is present as a homogeneous solution and on cooling a critical demixing temperature, below the critical demixing temperature in the liquid state of aggregation a miscibility gap, and a solidification temperature,
 - b) rendering the solution to form a shaped object, with first and second surfaces, in a die having a temperature above the critical demixing temperature,
 - c) cooling the shaped object using a cooling medium, conditioned to a cooling temperature below the solidification temperature, at such a rate that a thermodynamic non-equilibrium liquid-liquid phase separation into a high-polymer-content phase and a low-polymer-content phase takes place and solidification of the high-polymer-content phase subsequently occurs when the temperature falls below the solidification temperature,
 - d) possibly removing the low-polymer-content phase from the shaped object, characterized in that a solvent for the polymer component is selected for which, on cooling at a rate of 1°C/min, the demixing temperature of a solution of 25% by weight of the polymer component in this solvent is 10 to 70°C above the solidification temperature and that, for cooling, the shaped object is brought into contact with a liquid cooling medium that does not dissolve or react chemically with the polymer component at temperatures up to the die temperature.
 - 2. Process according to Claim 1, characterized in that the solvent for the at least one polymer is one for which, for a solution of 25% by weight of the polymer

component in this solvent and a cooling rate of 1°C/min, the demixing temperature is 20 to 50°C above the solidification temperature.

- 3. Process according to Claim 2, characterized in that the solvent for the at least one polymer is one for which, for a solution of 25% by weight of the polymer component in this solvent and a cooling rate of 1°C/min, the demixing temperature is 25 to 45°C above the solidification temperature.
- Process according to one or more of Claims 1 to 3, characterized in that the polymer component has a density of ≤ 910 kg/m³.
- 5. Process according to one or more of Claims 1 to 4, characterized in that the cooling medium is a non-solvent for the polymer component that, on heating up to the boiling point of the non-solvent, does not dissolve the polymer component to form a homogeneous solution.
- 6. Process according to one or more of Claims 1 to 5, characterized in that the cooling medium is a liquid that is a strong non-solvent for the polymer component and is homogeneously miscible with the solvent at the cooling temperature.
- 7. Process according to one or more of Claims 1 to 6, characterized in that the cooling medium has a temperature that is at least 100°C below the critical demixing temperature.
- 8. Process according to one or more of Claims 1 to 7, characterized in that 30-60% by weight of the polymer component is dissolved in 70-40% by weight of the solvent system.
- 9. Process according to one or more of Claims 1 to 8, characterized in that the at least one polyolefin contained in the polymer component consists exclusively of carbon and hydrogen.

- 10. Process according to Claim 9, characterized in that the at least one polyolefin is a poly(4-methyl-1-pentene).
- 11. Process according to Claim 9, characterized in that the at least one polyolefin is a polypropylene.
- 12. Process according to Claim 9, characterized in that the at least one polyolefin is a mixture of a poly(4-methyl-1-pentene) and a polypropylene.
- 13. Process according to Claim 10, characterized in that palm nut oil, dibutyl phthalate, dioctyl phthalate, dibenzyl ether, coconut oil, or a mixture thereof is used as the solvent.
- 14. Process according to Claim 11, characterized in that N,N-bis(2-hydroxyethyl)tallow amine, dioctyl phthalate, or a mixture thereof is used as the solvent.
- 15. Process according to one or more of Claims 1 to 14 for producing a hollow-fiber membrane.
- 16. Hydrophobic integrally asymmetrical membrane producible by a process according to one or more of Claims 1 to 15, wherein the membrane consists substantially of at least one polyolefin, has first and second surfaces and an intermediate support layer with a sponge-like, open-pored, microporous structure and adjacent to this support layer on at least one of its surfaces a separation layer, where the separation layer is dense or has pores with an average diameter < 100 nm, the support layer is free of macrovoids, the pores in the support layer are on average substantially isotropic, and the membrane has a porosity in the range from greater than 30% to less than 75% by volume.
- 17. Use of the membrane produced by a process according to one or more of Claims 1 to 15 for gas separation processes.

- 18. Use of the membrane produced by a process according to one or more of Claims 1 to 15 for gas transfer processes.
- Use of the membrane produced by a process according to one or more of Claims 1 to 15 for oxygenation of blood.
- 20. Use of the membrane according to Claim 16 for oxygenation of blood.